

REINFORCED REACTIVE MATERIAL

5 STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT

The invention described herein may be manufactured and used by or for the Government of the United States of America for government purposes without the payment of any royalties therefor.

10

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the field of reactive materials, and specifically to the field of reactive materials comprising composites of metals with polymers.

15

2. Description of the Related Technology

Several patents and publications are referred to herein, as illustrative of the contents of the art. These patents are incorporated by reference as if set forth fully herein.

20

Reactive materials are commonly used in military weaponry. These materials release amounts of thermal and/or percussive energy sufficient to cause a target's destruction. Reactive materials are typically delivered to targets via ordnance, that is, they are included in projectiles, such as shells or warheads. The projectiles may be launched from guns, cannons, or the like; alternatively, the projectiles may comprise

25

missiles, or may be delivered by missiles.

Reactive materials that have common military ordnance applications include, for example, gunpowder, trinitrotoluene (TNT), nitroglycerin, dynamite, fissile materials, and plastic explosives. It is also known to increase the destructive capability of ordnance by including shrapnel, and by shaping the charge to obtain a

30

desired pattern of energy release. Finally, it is known to calibrate the rate of destruction by varying the rate of energy released from the ordnance. Typically, this is achieved by selecting a reactive material with a reaction rate appropriate to the type of destruction required. For example, a highly energetic and largely percussive

explosion may be desirable to destroy certain targets, and a simple heat-induced fire may be suitable to destroy others.

Moreover, one or more reactive materials may be combined to create a desired destruction profile in a given type of ordnance. For example, the Office of Naval
5 Research is developing Reactive Materials Warheads (RMWs) to achieve complete and visible catastrophic structural defeat of cruise missiles and manned aircraft. The RMW is needed because, for example, an incoming missile may be hit and destroyed; however, its warhead may nonetheless remain intact and function independently on impact. The RMW, however, destroys its target to such an extent that any remaining
10 fragments of the target will not be independently dangerous.

The RMWs function by enhancing the kinetic energy of inert fragments, e.g., shrapnel, with chemical energy that is released when reactive fragments hit the target. The reactive fragments release heat and overpressure, thus adding to the destructive effect of the warhead fragments' kinetic energy as they strike the target. The reactive
15 fragments may include, for example, a reactive material designed to cling to the fragments of the target and release their chemical energy relatively slowly, over a time period on the order of several tenths of a second, for example.

Several examples of reactive materials likely to release chemical energy over a time period on the order of several tenths of a second are described in U.S. Patent
20 Nos. 6,485,586; 6,409,854; 6,402,864; 6,296,678; 6,293,201; and 4,432,816, for example.

Another desirable property for reactive materials to be used in a missile-delivered warhead is physical integrity sufficient to avoid excess deformation, melting or fragmentation under the temperature and pressure conditions of an explosive
25 launch. Physical integrity may be modeled by the strength or glass transition temperature (T_g) of a material.

As discussed above, most of the reactive materials commonly used in warheads are polymers or polymer composites. In general, these reactive materials are characterized by relatively low molecular weights and degrees of cross-linking.
30 As a result, their T_g and/or strength is inadequately low, resulting in insufficient physical integrity for purposes of explosive launch without additional containment features.

Means of increasing the strength and/or T_g of polymers are known in the art. For example, successful approaches have included crosslinking the polymer; increasing its molecular weight; blending with a polymer having favorable properties; co-polymerizing with monomers of a polymer having favorable properties; inclusion
5 of fibers or other structural reinforcement comprising carbon, ceramic, or a polymer having favorable properties (e.g., Kevlar™, available from E.I. du Pont de Nemours & Co. of Wilmington, DE); and using coupling agents to improve adhesion between the polymer and the included fibers. Applying these strategies to known reactive materials, however, while ensuring that their reactivity is not compromised, would
10 entail initiating expensive and time-consuming research programs.

In this connection, U.S. Patent No. 5,895,726 describes the impregnation of metal foams with a phthalonitrile prepolymer. The composite formed after curing the prepolymer is described as possessing superior structural properties; however, the composite is also said to be oxidatively stable and flame resistant, two properties that
15 indicate insufficient reactivity for use in a weapon's payload.

When a reactive material is lacking sufficient physical integrity for explosive launch, additional features must be added to a missile designed to deliver the reactive material. For example, the reactive material may be confined in a container, such as a steel box within the warhead. Additional containment features required to
20 compensate for inadequate physical integrity of the reactive material add expense and complication to the warhead.

There remains a need, therefore, for a reactive material that retains its physical integrity under the temperature and pressure conditions of an explosive missile launch.

25 Thus, it is an object of certain embodiments of the present invention to provide a reactive material with improved strength.

It is another object of certain embodiments of the present invention to provide a method for making a reactive material with improved strength.

30 These and other objects of the present invention will be apparent from the summary and detailed description of the invention, which follow.

SUMMARY OF THE INVENTION

In a first aspect, the invention relates to a reactive material comprising a metal foam and a polymer.

5 In a second aspect, the invention relates to a method of making a reactive material. The method comprises providing a metal foam, and imbibing a polymer into the metal foam.

In a third aspect, the invention relates to ordnance comprising a reactive material in accordance with the present invention or a reactive material made by the method of the present invention.

10

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is shows a schematic view of a metal foam including metal particles in the void volume of the metal foam.

15

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The term “reactive” as used herein, alone or in combined form, e.g., “reactive material”, refers to substances that generate intense heat and/or pressure when caused to react by heat, shock, radiation including light, pressure, friction, catalyst, or by contact with air or water. Examples of reactive materials include, without limitation, 20 explosive materials, polymerizing materials, oxidizers, water reactive materials, pyrotechnic substances, incendiary materials and pyrophores, and propellants.

A reactive material may include one or more components. When the reactive material includes more than one component, each component may or may not be reactive in its pure state.

25

The term “energetic” as used herein, alone or in combined form, e.g., “energetic material”, is synonymous with “reactive”.

The term “strength” as used herein, alone or in combined form, refers to the stress at which the a material takes a permanent set, that is, the material’s behavior is no longer elastic. Strength is measured in units of force per area.

30

The term “halogen” as used herein, alone or in combined form, e.g., metal halide, refers to fluorine, chlorine, bromine, or iodine.

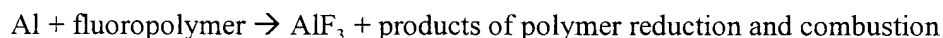
The term “foam” as used herein, alone or in combined form, refers to a structure that defines a void volume and is characterized by a relatively large internal surface area.

5 The term “imbibe” as used herein, alone or in combined form, e.g., “imbibable”, refers to placing a substance within a structure. It is to be understood that, after imbibing a substance into a structure, any voids that are present in the structure may be completely or partially filled with the substance. Examples of imbibing include, without limitation, placing solids or liquids within the voids of a foam.

10 In a first aspect, the present invention relates to reactive materials which include a metal foam and a polymer.

Preferred reactive materials for use in the present invention include combinations of metals and halogenated polymers. The reactivity of these combinations is based on the large, negative enthalpy of formation of metal halides.

15 In one example of a suitable reaction,



20 The enthalpy of formation of aluminum (III) fluoride is -313 kcal/mol. This highly exothermic reaction contributes to the reactivity of a mixture of aluminum and polytetrafluoroethylene (PTFE), for example.

Any polymer that can form a reactive material with a metal is suitable for use in the present invention. The polymer may be independently reactive, provided its reactivity is not adversely affected to a significant extent by the metal foam
25 component of the reactive material, for example, nitrocellulose or guncotton may be suitable for use in the present invention. The polymer may be a component of a reactive composition that is capable of being imbibed into a metal foam, for example, so-called “plastic explosives” and the like, including “Semtex”, a mixture of RDX (cyclotrimethylenetrinitramine), PETN (pentaerythritol tetranitrate), poly(butadiene-
30 styrene), and oil. Alternatively, the polymer may be reactive only in combination with the metal, for example, Teflon™ PTFE, Viton™ fluoroelastomer, and other

halogenated polymers. Mixtures of two or more different polymers may also be employed.

In general, halogenated polymers are preferred for use in the present invention. Preferred halogens include fluorine and chlorine, because they are less expensive, and because metal fluorides and chlorides usually have especially favorable enthalpies of formation. Halogenated polymers may be partially or fully halogenated. Fully halogenated polymers are polymers wherein the maximum number of hydrogen atoms are replaced by halogens. Partially halogenated polymers are those wherein some hydrogen atoms are replaced by halogens, but wherein it would be chemically feasible to replaced additional hydrogen atoms with halogens, if desired.

Preferred halogenated polymers are formed from one or more of the following monomers: fluoroalkyl esters of acrylic acid, tetrafluoroethylene, chlorotrifluoroethylene, dichlorodifluoroethylene, hexafluoropropylene, vinylidene dichloride, vinylidene difluoride, and the like. Polymers formed from a mixture of two or more monomers may be employed in the present invention. Such polymers may include mixtures of two or more monomers which provide groups reactive with the metal foam, e.g. halogens, or such polymers may be formed from a mixtures of one or more monomers which provide reactive groups and one or more monomers which do not provide groups reactive with the metal foam. Thus, the structural integrity of the material could be further enhanced by incorporating certain monomers into the polymer in this manner. Also, the use of mixtures of two or more polymers could provide the ability to tailor the energy release from the reactive material by, for example, providing a situation wherein two or more chemical reactions between the polymer and metal foam have different reaction rates.

More preferably, the polymer consists essentially of one or more of the following monomers: fluoroalkyl esters of acrylic acid, tetrafluoroethylene, chlorotrifluoroethylene, dichlorodifluoroethylene, hexafluoropropylene, vinylidene dichloride, vinylidene difluoride, and the like.

Particularly preferred halogenated polymers include, or more preferably consist essentially of, highly fluorinated polymers such as Teflon™ (PTFE).

In general, a metal is suitable for use in the present invention if it can be formed into a foam whose strength is sufficient, when combined with other materials

to form the reactive material, to maintain structural integrity when subjected to loading, for example, on explosive launch. As discussed above, reactive materials may be delivered to a target in a variety of different ways. Thus, the metal foam component of the present invention is designed to provide sufficient structural integrity, when combined with other materials to form the reactive material, to withstand the loading to which the reactive material will be subjected for a particular delivery method.

Preferably, the enthalpy of formation of the corresponding metal halides is sufficiently negative for the metal to form a reactive material in combination with a halogenated polymer. Preferably, the metal is selected from the group consisting of molybdenum, osmium, titanium, boron, manganese, magnesium, aluminum, and nickel. Aluminum is a particularly preferred metal and a particularly preferred metal foam consists essentially of aluminum. The metal may also be in the form of an alloy containing one or more of the metals listed above.

The metal foams may be made by any known method for forming metal foams, such as, for example, those described in U.S. Patent Nos. 3,940,262; 3,981,720; 4,569,821; and other methods that are known to those of skill in the art.

In addition to increasing the strength of the reactive material, the metal foam provides a relatively large contact area between the metal and the polymer in the polymer-metal mixture, thereby favoring the kinetics of the reaction between the metal and the polymer. Consequently, it is desirable that the metal foam be characterized by a relatively large surface area. Preferably, the metal foam employs the maximum surface area obtainable for a given suitable, predetermined strength. Also, it is preferable that the metal foam contain sufficient internal void volume to permit at least a stoichiometric amount of the polymer to be imbibed into the void volume of the metal foam.

The void volume of the metal foam is also preferably substantially contiguous, so that a vacuum applied to a portion of the structure can cause a significant amount of polymer to be drawn into the foam. Likewise, in an alternative method of synthesizing the reactive materials of the invention, a positive pressure may be used to drive a significant amount of polymer into the foam, in which case the void volume of the metal foam is also preferably substantially contiguous. Other process parameters

that may be relevant to making an aluminum/PTFE containing reactive material are set forth in U.S. Patent No. 6,547,993.

The amount of polymer employed relative to the metal foam may be determined based on a number of factors. For example, it is desirable to provide an amount of polymer that maximizes the energy output of the reaction between the polymer and the metal foam. This amount may depend on the stoichiometry of the reaction between the polymer and the metal foam, the surface area of the metal foam and the conditions under which the reaction between the polymer and metal foam will take place. Other factors to be considered in determining the appropriate amount of polymer will be the void volume of the metal foam, the degree to which the amount of polymer may affect the overall structural integrity of the reactive material, and other materials that may be included in the reactive material. For example, it may be desirable to employ a larger amount of polymer than required by the stoichiometry of the reaction between the polymer and the metal foam, if additional reactive metal not forming part of the foam is included in the reactive material.

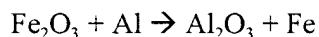
Typically, the amount of polymer and metal employed in the reactive metal is from about 65% to about 85% polymer and about 15% to about 35% metal. The relative amounts of the polymer and metal employed in a specific embodiment of the invention will depend, to some extent, on the particular polymers and metals employed in that embodiment.

Other materials may optionally be included in the reactive material of the present invention. For example, it may be desirable to add finely divided metal particles to the polymer. The finely divided metals may be useful to improve the stoichiometry of the reaction between the metal foam and the polymer, for example, when the mass of the polymer is too great to react completely with the metal foam. Also, the use of finely divided metals can potentially increase the surface contact area between the polymer and the reactive metal by providing contact area between the polymer and the finely divided metal in addition to the contact area between the polymer and the surface of the metal foam. The finely divided metal particles preferably contain one or more of the metals listed above which are suitable for use in the metal foams of the present invention.

Referring to Fig. 1, there is shown a schematic view of a metal foam matrix 10, having void volume 12. Within the void volume 12 of the metal foam matrix 10 is shown metal particles 14.

Also, it may be desirable in some instances to include finely divided metal oxide particles in the polymer. The finely divided metal oxide particles preferably contain metal oxides that are reactive with the polymer in order to adjust the energy output from the reactive material. Metal oxide particles can also be used, for example, to tailor the energy output of the reactive material by providing a second, different energy-producing reaction in the reactive material, in addition to the reaction between the polymer and the metal foam. The metal oxide particles preferably contain metal oxides, which are capable of undergoing an exothermic reaction with the polymer. Suitable metal oxides are known to persons skilled in the art and may include, for example, oxides of molybdenum, osmium, titanium, boron, manganese, magnesium, aluminum, and nickel.

Alternatively, the finely divided metal powder may form one component of a thermite mixture, which is a combination of a metal and a metal oxide. In the thermite reaction, the metal oxide is reduced to an elemental metal, and the metal starting material is oxidized. Often, the thermite reaction is highly exothermic. For example, one well-known thermite reaction is:



The enthalpy of this reaction is -203 kcal/mol , and the iron metal product is typically molten. It is thus apparent that the reactivity of the energetic material of the invention may be improved by including a thermite mixture.

It may be desirable to include oxidizing salts in the reactive material of the present invention. Examples of oxidizing salts are described in U.S. Patent Nos. 3,753,811 and 3,513,043, e.g.

It may also be desirable to include plasticizers in the reactive materials of the present invention. The plasticizers may be reactive, such as those described in U.S. Patent No. 6,325,876, or nonreactive.

Other additives that may be used in the compositions of the present invention include binders and other miscellaneous additives. Examples of other additives are a 50/50 mixture of bis(2,2-dinitropropyl)acetal/ bis(2,2-dinitropropyl)formal, amorphous silicon oxides such as Cab-O-Sil® M-5, tris-β-chloroethyl-phosphate, diocetylphthalate, polyurethanes such as Estane® 57-2-F1, vinyl chloride/chlorotrifluoroethylene copolymer in a 1.5/1 ratio of monomers such as FPC® 461, chlorotrifluoroethylene/vinylidene fluoride copolymer in a 3:1 ratio of monomers, such as Kel-F® 800, polystyrene, poly(dimethylsiloxanes) such as Sylgard® 182, and vinylidene fluoride/hexafluoropropylene copolymer in a ratio of 60%/40% such as Viton® A.

In another aspect, the present invention relates to a method of making a reactive material comprising a polymer and a metal. The method of the present invention comprises providing a metal foam and imbibing a polymer into the metal foam. As noted above, the polymer may be imbibed into the metal foam by any suitable method for filling the void volume of a foam with a polymer, using, for example, positive pressure, a vacuum, and polymer powder, melt, or solution. Preferably, when vacuum is applied, at least a portion of the void volume of the metal foam is held under vacuum as the polymer is imbibed into the void volume of the metal foam. When positive pressure is applied, at least a portion of the polymer is preferably imbibed into the void volume of the metal foam while positive pressure is applied to the polymer.

The polymer may be imbibed into the void volume of the metal foam in any suitable form. Preferably, the polymer is imbibed into the void volume of the metal foam in the form of a powder or liquid. Imbibing the polymer into the metal foam in the form of a polymer melt is preferred and is generally applicable since the polymeric materials tend to have significantly lower melting points than the metals contained in the metal foam, thereby allowing the polymer to be contacted with the metal foam in the melt form without adversely affecting the structural properties of the metal foam.

The method of the present invention can be used to provide increased strength to the reactive material, relative to a reactive material consisting of a mixture of the same polymer and the same metal provided in the form of finely divided metal particles. The increased strength of the reactive material is provided with little or no

reduction in the energy output of the reactive material since the metal foam provides a relatively large contact area between the polymer and the reactive metal and because it is still possible to add additional reactive metal in the form of, for example, finely divided metal to the reactive material of the present invention to further enhance the energy output.

In a first preferred method in accordance with the present invention, a metal foam is provided. Air is evacuated from all or a substantial portion of the void volume of the metal foam and polymer is melted and imbibed into the void volume of the metal foam. The polymer and metal foam are then consolidated by cooling.

Another preferred method in accordance with the present invention may be employed if an additional metal powder is to be incorporated into the reactive material. In this method, a metal foam is provided and air is evacuated from all or a substantial portion of the void volume of the metal foam. The polymer is melted and mixed with the additional metal powder, preferably using sufficient mixing to provide an intimate mixture of metal powder and melted polymer. Alternatively, the polymer and metal powder can initially be mixed in powder form and subsequently the polymer can be melted. The melted polymer and metal powder mixture is then imbibed into the void volume of the metal foam. Once the melted polymer is imbibed into the void volume, the metal foam and polymer/metal powder mixture may be consolidated by cooling or by compressing the metal foam and polymer/metal powder mixture and then cooling.

All of the various types of polymers, metals, and optional additives described above for the reactive material of the present invention, may also be employed in the methods of the present invention. Thus, the optional additives are preferably imbibed into the void volume of the metal foam in the form of a mixture with the polymer.

Also provided by the present invention is ordnance including a reactive material comprising a polymer and a metal foam. Methods of making ordnance are well known to those of skill in the art. Examples of such techniques may be found in Joseph Carleone, Ed.; *Tactical Missile Warheads, Progress in Astronautics and Aeronautics*, Vol. 155, American Institute of Aeronautics and Astronautics, 1993; Lloyd, R., *Conventional Warhead Systems Physics and Engineering Physics and Engineering Design*, Progress in Astronautics and Aeronautics, Vol. 179, American

Institute of Aeronautics and Astronautics, 1998; and Lloyd, R. *Overview of Kinetic Energy Rod Warhead Technology*, Multinational Conference on Theater Missile Defence, Munich, Germany, June 1996. More advanced techniques, such as forming shaped charges, fragmentation warheads, etc., may also be used in ordnance of the present invention.

The reactive material of the present invention is characterized by a relatively high degree of structural integrity. As a result, when the reactive material of the present invention is incorporated into ordnance, it may be possible to avoid using additional structure in the ordnance to maintain the structural integrity of the reactive material. For example, in some applications, reactive material must be encased in an additional canister to protect it from the stresses to which it is subjected upon, for example, launch. The present invention may permit the fabrication of suitable ordnance without using additional structure to protect the reactive material.

In addition, the reactive material of the present invention could be used to replace part or all of one or more structural elements in ordnance to thereby increase the overall energy output of that ordnance relative by inclusion of additional reactive material therein.

Ordnance in accordance with the present invention may contain one or more of the same optional ingredients that may be incorporated into the reactive material, as described above. Ordnance in accordance with the present invention preferably contains reactive material made by one of the methods of the present invention.

The invention will be further illustrated by the following example, which is not to be construed as limiting the invention in any way.

EXAMPLE

The strength of a suitable polymer was 3200 psi. The strength of aluminum was 30,000 psi. An aluminum foam with 96% void volume was used. The strength of the composite material formed by the polymer and the aluminum foam was

$$0.96(3200 \text{ psi}) + 0.04(30,000 \text{ psi}) = 4272 \text{ psi}$$

Thus, the inclusion of the aluminum foam increases the strength of the composite by 33.5% over the strength of the polymer alone. The increase in strength due to the aluminum foam is more significant at elevated temperatures, because the

strength of the polymer decreases more rapidly than the strength of the aluminum with increasing temperature.

5 Assuming that the material is elastic-perfectly plastic, the ultimate strength is achieved when both materials carry their maximum load. The strength relationship is linear until the first material yields, then a second linear relationship occurs until the second material fails. However, in reality, since the aluminum is less elastic than the polymer, the aluminum will yield first, but its higher strength will allow the aluminum to carry additional load until the polymer yields.

10 Changes may be made in carrying out the methods and to the compositions of the invention above set forth above without departing from the spirit and scope of the invention. It is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense. The scope of this invention is to be determined from the claims appended hereto.